

This Page Is Inserted by IFW Operations
and is not a part of the Official Record

BEST AVAILABLE IMAGES

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images may include (but are not limited to):

- BLACK BORDERS
- TEXT CUT OFF AT TOP, BOTTOM OR SIDES
- FADED TEXT
- ILLEGIBLE TEXT
- SKEWED/SLANTED IMAGES
- COLORED PHOTOS
- BLACK OR VERY BLACK AND WHITE DARK PHOTOS
- GRAY SCALE DOCUMENTS

IMAGES ARE BEST AVAILABLE COPY.

**As rescanning documents *will not* correct images,
please do not report the images to the
Image Problem Mailbox.**

PATENT ABSTRACTS OF JAPAN

(11)Publication number : 09-266113

(43)Date of publication of application : 07.10.1997

(51)Int.Cl.

H01F 10/08

C22C 38/00

H01F 1/147

H01F 41/22

(21)Application number : 08-075734

(71)Applicant : HITACHI METALS LTD

(22)Date of filing : 29.03.1996

(72)Inventor : SAKUMA AKIMASA
SHINDO MIKIO
TOKUNAGA MASAACKI

(54) HARD MAGNETIC THIN FILM AND EXCHANGE SPRING MAGNET, AND THEIR MANUFACTURE

(57)Abstract:

PROBLEM TO BE SOLVED: To increase magnetization, and hence ensure a hard magnetic thin film and an exchange spring magnet both being excellent in performance and both having a maximum energy product, by exchangeably coupling a hard magnetic layer and a soft magnetic layer, and forming a laminate film where there are alternately laminated a specific range thickness hard magnetic layer and a specific range soft magnetic layer.

SOLUTION: There are exchangeably coupled a hard magnetic layer which uses as a main structure of any one of crystal structures of the types of CaCu_5 , TbCu_7 , Gd_2Co_7 , or Ce_2Ni_7 , ThMn_{12} , $\text{Th}_2\text{Zn}_{17}$ or $\text{Th}_2\text{Ni}_{17}$, or a composite thereof and a soft magnetic layer using a soft magnetic material where the magnitude of magnetization is 1.3T at room temperature, and hereby a laminate film is ensured where a 1nm to 700nm hard magnetic layer and a 1nm to 700nm thick soft magnetic layer are alternately laminated. As a result, there are ensured a hard magnetic thin film and an exchange spring magnet which are excellent in performance and which has greater magnetization and a maximum energy product.

LEGAL STATUS

[Date of request for examination]

13.02.2003

[Date of sending the examiner's decision of rejection]

[Kind of final disposal of application other than the examiner's decision of rejection or application converted registration]

[Date of final disposal for application]

[Patent number]

[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

Copyright (C); 1998,2003 Japan Patent Office

*** NOTICES ***

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1. This document has been translated by computer. So the translation may not reflect the original precisely.

2. **** shows the word which can not be translated.

3. In the drawings, any words are not translated.

CLAIMS

[Claim(s)]

[Claim 1] A hard magnetism thin film characterized by being the cascade screen to which a hard magnetism layer and a soft magnetism layer became from a composite construction which carried out switched connection, and the laminating of a hard magnetism layer with a thickness of 1nm - 700nm and the soft magnetism layer with a thickness of 1nm - 700nm was carried out by turns.

[Claim 2] a hard magnetism layer -- RaTMbNMcADdXe (inside of rare earth elements with which R contains Y -- at least -- a kind and TM -- inside of Fe, Co, and nickel -- at least -- a kind --) A kind and X of a kind and AD at least are kinds at least among boron, carbon, or nitrogen inside among aluminum, Zn, Cu, Ga, germanium, Zr, Nb, Sn, Sb, Hf, and Ta. NM -- Si, Ti, V, Cr, Mo, W, and ** -- $5 \leq a \leq 18\text{at\%}$ and $65 \leq b \leq 85\text{at\%}$ and $0 \leq c \leq 20\text{at\%}$ and $0 \leq d \leq 8\text{at\%}$ and $0 \leq e \leq 15\text{at\%}$ -- a hard magnetism thin film according to claim 1 which has a presentation.

[Claim 3] A hard magnetism thin film according to claim 1 or 2 with which a hard magnetism layer has a presentation of RaTMbNMcADdXe, and makes main structure any of CaCu5 mold, TbCu7 mold, Gd2Co7 mold or Ce2nickel7 mold, ThMn12 mold, Th2Zn17 mold, or the Th2nickel17 mold crystal structure, one, or these complex.

[Claim 4] A hard magnetism thin film given in claim 1 thru/or any of 3 they are. [whose magnitude of magnetization of a soft magnetism layer is more than 1.3T in a room temperature]

[Claim 5] A hard magnetism thin film given in claim 1 thru/or any of 4 they are. [which has a protective coat which consists of M layers on the surface of a cascade screen]

[Claim 6] An exchange spring magnet characterized by a hard magnetism layer with a thickness of 1nm - 700nm and a soft magnetism layer with a thickness of 1nm - 700nm consisting of a cascade screen by which the laminating was carried out by turns.

[Claim 7] A hard magnetism thin film according to claim 6 which has a protective coat which consists of M layers on the surface of a cascade screen.

[Claim 8] A manufacture method of an exchange spring magnet characterized by heat-treating at temperature of 773K (500 degrees C)-1073K (800 degrees C) at substrate temperature below 773K (500 degrees C) on a substrate after forming a soft magnetism layer and at least one or more layers of hard magnetism layers.

[Translation done.]

*** NOTICES ***

Japan Patent Office is not responsible for any damages caused by the use of this translation.

1.This document has been translated by computer. So the translation may not reflect the original precisely.

2.**** shows the word which can not be translated.

3.In the drawings, any words are not translated.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[The technical field to which invention belongs] This invention relates to the thin film magnet, the R-TM-B system exchange spring magnet, and its manufacture method of the multilayer structure to which the laminating of the R-TM-B system hard magnetism layer applied to a small motor, a magnetometric sensor, an actuator, etc. and the soft magnetism layer was carried out.

[0002]

[Description of the Prior Art] High performance-ization of a permanent magnet material is advanced corresponding to small and lightweight-izing of an electronics device. An exchange spring magnet is mentioned as an example of the material which may exceed the magnetic properties of the R-TM-B system magnet which has current and the highest magnet property. Magnetization of a hard magnetism phase fixes magnetization of a soft magnetism phase, and the coercive force of an exchange spring magnet discovers it by barring the flux reversal of a soft magnetism phase. In order to acquire sufficient coercive force, it is required that the soft magnetism phase and the hard magnetism phase are carrying out switched connection strongly and for the magnitude (particle size) of each phase to be nano level size. The manufacture method of this exchange spring magnet has a method in use of obtaining the polycrystal which manufactured the amorphous thin band with the super-quenching method, and the soft magnetism phase and the hard magnetism phase mixed by heat treatment.

[0003]

[Problem(s) to be Solved by the Invention] Since the magnet of the electronics device by which buildup of need will be expected from now on is asked more for small, lightweight-izing, and high performance-ization, still bigger magnetization than a current Nd-Fe-B system magnet comes to be required, and development for the cure or retrieval of a new magnet is advanced. This invention offers the outstanding hard magnetism thin film which has a big maximum energy product by having big magnetization, a rare earth system exchange spring magnet, and its manufacture method.

[0004]

[Means for Solving the Problem] permanent magnet which consists of super-fine crystal organizations which consist of a two phase of a hard magnetism phase and a soft magnetism phase Coehoorn etc. (J. dePhys.vol.49, p669 (1988)) etc. -- Kneller etc. (IEEE Trans.Mag.vol.27, p3588 (1991)) etc. -- it is proposed and is called an exchange spring magnet. This will acquire a high energy product by combining a large soft magnetism phase of magnetization, and a large hard magnetism phase of coercive force generally, and combining these magnetically by exchange interaction. Generally, if there is a soft magnetism phase which carries out switched connection to a hard magnetism phase in permanent magnet material, flux reversal will begin from a soft magnetism phase previously under an opposing magnetic field, and it will become the key factor of coercive force lowering. However, if size of a soft magnetism phase is held down to below magnetic domain wall width of face, ununiformity flux reversal under an opposing magnetic field will be controlled. Consequently, coercive force is mainly governed by the magnetic anisotropy of a hard magnetism phase, and lowering is suppressed. What is necessary is on the other hand, to raise a volume ratio of a soft magnetism phase and for that just to make size of one hard magnetism phase as small as possible, in order to obtain the higher flux density B from a soft magnetism phase. Although size of a hard

magnetism phase should just be below magnetic domain wall width of face too, since it will become difficult to maintain coercive force if not much narrow, it is desirable to hold down to a magnetic domain wall width-of-face degree. Since magnetic domain wall width of face is estimated by $\pi(A/K) 1/2$ (A: exchange SUTIFFUNESU constant, K: anisotropy energy), if a soft magnetism phase is set to Fe and a hard magnetism phase is set to Nd₂Fe₁₄B, it will be set to 60nm and about several nm, respectively. R. According to Skomski and J.M.D. Coey (Phys.Rev.B48(1993) p15812), in an exchange spring magnet, the volume ratio f_h of a hard magnetism phase in case maximum energy product (BH) max becomes the largest is given by (1) formula in approximation, and a maximum energy product serves as (2) types at this time.

[0005]

[Formula 1]

$$f_h = \frac{\mu_0 M_s^2}{4 K_h} \quad (1)$$

(M_s : 軟磁性相の磁化、 K_h : 硬磁性相の磁気異方性エネルギー)

$$(BH)_{max} = \frac{\mu_0 M_s^2}{4} \left(1 - \frac{\mu_0 (M_s - M_h) M_s}{2 K_h} \right) \quad (2)$$

(M_h : 硬磁性相の磁化)

[0006] Generally, to the anisotropy energy K_h of Sm-Co or a Nd-Fe-B magnet being about [107J //m] three, since $\mu_0 M_s 2/4$ of soft magnetic materials, such as Fe, is about three 106 J/m, it should just have about 10% of volume ratios f_h of a hard magnetism phase. Therefore, (BH) max serves as a form where the property of a soft magnetism phase mainly rules over, and slight amendment joins $\mu_0 M_s 2/4$ quantitatively. (2) When Nd₂Fe₁₄B is made into a hard magnetism phase and Fe is made into a soft magnetism phase in a formula, (BH) max=0.8 MJ/m³ (100MGOe) is expected at $f_h=10\%$. In order to acquire the above properties, it has magnetic association with a hard magnetism phase and a soft magnetism phase sufficient by contact interface, and needs to be controlled by magnetic domain wall width-of-face degree which each phase thickness mentioned above. It is thought that a cascade screen set as the object of this invention is the structure where such control may be realized most easily.

[0007] A hard magnetism layer which consists of R-TM-NM-AD-X has a high possibility that will become, or switched connection with a soft magnetism phase will serve as [an intermetallic compound containing rare earth] imperfection being hard to generate, and coercive force will deteriorate, if corrosion resistance is bad and does not fully control oxidation. By applying a thin film technology, structure was made easy to control, and this invention person etc. raised coercive force, and hit on an idea by forming a protective coat for oxidation control by thin-film-izing to prevent lowering of coercive force. Therefore, this invention consists of a composite construction in which a hard magnetism layer and a soft magnetism layer carried out switched connection, and a hard magnetism layer with a thickness of 1nm - 700nm and a soft magnetism layer with a thickness of 1nm - 700nm are the hard magnetism thin films which are cascade screens by which the laminating was carried out by turns. this invention -- setting -- a hard magnetism layer -- RaTbNbMcADdXe (inside of rare earth elements with which R contains Y -- at least -- a kind and TM -- inside of Fe, Co, and nickel -- at least -- a kind --) A kind and X of a kind and AD at least are kinds at least among boron, carbon, or nitrogen inside among aluminum, Zn, Cu, Ga, germanium, Zr, Nb, Sn, Sb, Hf, and Ta. NM -- Si, Ti, V, Cr, Mo, W, and ** -- $5 \leq a \leq 18\text{at\%}$ and $65 \leq b \leq 85\text{at\%}$ and $0 \leq c \leq 20\text{at\%}$ and $0 \leq d \leq 8\text{at\%}$ and $0 \leq e \leq 15\text{at\%}$ -- it has a presentation. A hard magnetism layer can make main structure any of CaCu₅ mold, TbCu₇ mold, Gd₂Co₇ mold or Ce₂Ni₁₇ mold, ThMn₁₂ mold, Th₂Zn₁₇ mold, or the Th₂Ni₁₇ mold crystal structure, one, or these complex. It is desirable that magnitude of magnetization uses soft magnetic materials which are more than 1.3T in a room temperature as a soft magnetism layer. Moreover, this invention is the rare earth system exchange spring magnet which carried out the laminating of a soft magnetism layer with a thickness of 1nm - 700nm and the hard magnetism layer with a thickness of 1nm - 700nm. In this invention, in order to carry out switched connection of a soft magnetism layer and

the hard magnetism layer, it is desirable to carry out the laminating of a soft magnetism layer and the hard magnetism layer by turns, and to consider as a multilayer. Moreover, it is desirable to form M layers (layer which consists of one sort or two sorts or more in Cr, Ti, W, Cu, V, Ta, FeMn, NiMn, NiO, FeO and CoO, Co-Pt, and Fe-Pt) in a front face of a multilayer which carried out the laminating of a soft magnetism layer and the hard magnetism layer, and to control oxidation of a soft magnetism layer and a hard magnetism layer.

[0008] this invention — setting — a hard magnetism layer — $RaTbMnMcADdXe$ (inside of rare earth elements with which R contains Y — at least — a kind and TM — inside of Fe, Co, and nickel — at least — a kind —) NM — Si, Ti, V, Cr, Mo, W, and ** — a kind and X at least at least a kind and AD inside among aluminum, Zn, Cu, Ga, germanium, Zr, Nb, Sn, Sb, Hf, and Ta inside of boron, carbon, or nitrogen — at least — a kind — $5 \leq a \leq 18\text{at\%}$ and $65 \leq b \leq 85\text{at\%}$ and $0 \leq c \leq 20\text{at\%}$ and $0 \leq d \leq 8\text{at\%}$ and $0 \leq e \leq 15\text{at\%}$ — it is desirable that it is the hard magnetism thin film which has a presentation. Especially as R, it is desirable to include at least one sort of Nd, Sm, or Pr, and a part of Nd, Sm, or Pr may be replaced by Dy. Thickness sets to 1–700nm a hard magnetism layer which consists of R-TM-NM-AD-X including any of CaCu_5 mold, TbCu_7 mold, Gd_2Co_7 mold or $\text{Ce}_2\text{nickel}_7$ mold, ThMn_{12} mold, $\text{Th}_2\text{Zn}_{17}$ mold, or the $\text{Th}_2\text{nickel}_{17}$ mold crystal structure, one, or these complex, and its 5–100nm is more desirable. a hard magnetism layer — R — coercive force sufficient less than [5at%] — not discovered — more than 18at% — TM component — decreasing — (BH) — max and Br decrease. Addition of NM is effective for the crystal stability of a rare earth intermetallic compound, and becomes indispensable to formation of a ThMn_{12} mold crystal especially. however, more than 20at% — addition causes remarkable lowering of Br. AD has an effect in detailed-izing of crystal grain of a formed rare earth intermetallic compound, and equalization, and is effective for reservation of holding power. X — buildup of Br — effective — more than 15at% — (BH) — max and Br fall.

[0009] Since magnetization of a hard magnetism layer which consists of R-TM-NM-AD-X is usually more than 1.3T at a room temperature, in order to acquire the predominance of an exchange spring magnet, in order to carry out to more than 1.3T at a room temperature and to exceed the property of a R-Fe-B system magnet of bulk further, as for magnitude of magnetization of a soft magnetism layer, it is desirable to carry out to more than 1.5T. As soft magnetic materials beyond 1.3T, Fe:2T, Fe-Co:2.3T, and Fe-N:2.4T grade have the magnitude of magnetization in a room temperature. As for a soft magnetism layer, it is desirable to think from width of face of the magnetic domain wall, and for it to be referred to as 1–700nm, and to be referred to as 5nm – 500nm. Although a multilayer which carried out the laminating of a soft magnetism layer and the hard magnetism layer by turns is formed in order to carry out switched connection of a hard magnetism layer and the soft magnetism layer the order of a laminating — a soft magnetism layer, a hard magnetism layer, a soft magnetism layer, and ..., even if it carries out a laminating to a soft magnetism layer a hard magnetism layer, a soft magnetism layer, a hard magnetism layer, and ... even if it carries out a laminating to a hard magnetism layer — a soft magnetism layer, a hard magnetism layer, a soft magnetism layer, and ... even if it carries out a laminating to a hard magnetism layer — a hard magnetism layer, a soft magnetism layer, a hard magnetism layer, and ... a laminating may be carried out to a soft magnetism layer, or any are sufficient.

[0010] M layers (layer which consists of one sort or two sorts or more in Cr, Ti, W, Cu, V, Ta, FeMn, NiMn, NiO, FeO and CoO, Co-Pt, and Fe-Pt) are formed in the outermost side of a multilayer which carried out the laminating of a soft magnetism layer and the hard magnetism layer by turns, and oxidation of a soft magnetism layer and a hard magnetism layer is controlled. M layers may be formed in one of the two so that you may form all over the front face of a cascade screen and a multilayer may be inserted. Although an effect of oxidation control is acquired also by forming M layers between a substrate and a multilayer and in either on a cascade screen of a soft magnetism layer and a hard magnetism layer, by forming so that the whole surface surface or a multilayer may be inserted, oxidation of a soft magnetism layer and a hard magnetism layer can be controlled enough, consequently switched connection of a hard magnetism layer and a soft magnetism layer becomes strong, and a multilayer which was excellent in magnetic properties can be obtained. Moreover, an effect of preventing oxidation control of a soft magnetism layer or a hard

magnetism layer and a reaction with a substrate is acquired by forming M layers on a substrate and carrying out the laminating of the multilayer of a soft magnetism layer and a hard magnetism layer on it. 5nm – 100nm of thickness of M layers is desirably set to 5–20nm so that the function may not fully be spoiled, even if it forms an alloy or a compound by interface by counter diffusion with a hard magnetism layer or a soft magnetism layer which adjoins this.

[0011] Since NiO, FeO, and CoO are antiferromagnetism insulating materials, if this is used as M layers; in addition to an effect of oxidation control, an effect of improvement in coercive force can be acquired by stopping flux reversal. Although an effect of improvement in coercive force can be acquired if this is used as M layers since FeMn and NiMn are also the antiferromagnetic substance, it is desirable to compare with other M layer constituents, and to form between a substrate, a hard magnetism layer, or a soft magnetism layer, since there are few antioxidizing effects. Moreover, since Co–Pt and Fe–Pt are ferromagnetic metals which have a strong crystal magnetic anisotropy, if this is used as M layers, in addition to the antioxidizing effect and an effect of coercive force buildup, they can also expect buildup of magnetization.

[0012] Although it is desirable to form membranes at substrate temperature below 773K (500 degrees C) as for a hard magnetism layer in order to control oxidation at the time of membrane formation of a hard magnetism layer, a hard magnetism layer which consists of R–TM–NM–AD–X in that case has become amorphous, without crystallizing, and coercive force does not discover it. In this case, heat treatment is required in order to obtain polycrystal of a rare earth intermetallic compound. Since a compound will not crystallize heat treatment temperature if it is made below into 773K (500 degrees C), if coercive force is not discovered and it carries out more than 1073K (800 degrees C), coercive force will decrease rapidly. therefore, turbulence of a laminated structure by diffusion under heat treatment although 773K (500 degrees C) to 1073K (800 degrees C) are suitable for heat treatment temperature -- few -- and ** -- enough -- 773K (550 degrees C) to 923K (650 degrees C) to generate are desirable.

[0013]

[A mode of implementation of invention]

(Example 1) The inside of a vacuum tub of bipolar magnetron sputtering equipment was exhausted to 8×10^{-4} or less Pa, and Ar gas was introduced, it was referred to as 8×10^{-1} Pa, and Ta film was first produced as M layers on the following membrane formation conditions by using Ta as a target. Glass substrate temperature of 25 degrees C and a shutter attached between a substrate and a target before membrane formation as RF charge power 200W were closed, and a reserve spatter removed an oxide on a target for 5 minutes. Next, a shutter was opened and 10nm of Ta was formed by membrane formation speed 1.3 micrometer/h. Next, membranes were formed so that SmCo₅ might serve as a hard magnetism layer. Membrane formation conditions are RF charge power 200W, and performed a reserve spatter for 20 minutes for scaling object clearance of SmCo_{4.5} target. Next, 10nm of SmCo(es)₅ was formed by membrane formation speed 2.0 micrometer/h. Without breaking a vacuum succeedingly, high-frequency voltage was impressed to Fe target, and 10nm of Fe films was formed on SmCo₅ and these conditions. Membrane formation speed is 0.3 micrometer/h. This was repeated by turns, a multilayer (ten laminatings) of SmCo₅ and Fe was produced, and, finally 20nm of V films was produced. A SmCo₅/Fe multilayer protected by Ta film and V film which were obtained was heat-treated by 600C \times 0.5h and 3×10^{-3} Pa. Acquired magnetic properties were Br=0.95T, iHc=159 kA/m, and (BH) max=135 kJ/m³. Moreover, since the so-called springback which 75% of magnetization restores was accepted when a demagnetizing field equivalent to iHc was impressed to an obtained hard magnetism thin film and a recoiling property was investigated, it was checked that this magnetic film is an exchange spring magnet.

[0014] (Example 2) 20nm of Ti was formed on a glass substrate, and a Sm–Co–Fe–Cu–Zr/Fe–Co multilayer (ten laminatings) was formed by the method as an example 1 that next it is the same. Finally 20nm of Ti was formed again. A hard magnetism layer is Sm (Cobal.Fe_{0.2}Cu_{0.05}Zr_{0.02})₇, and a soft magnetism layer is a 70wt%Fe–30wt%Co presentation. An obtained multilayer was heat-treated by 600C \times 0.5h and 3×10^{-3} Pa. Acquired magnetic properties were Br=1.0T, iHc=120 kA/m, and (BH) max=155 kJ/m³.

[0015] (Example 3) 20nm of Ti was formed by the method as an example 1 that it is the same on a glass substrate. Next, a membrane formation ambient atmosphere was changed to 5% of nitrogen, and Ar95%, and

10nm of Sm₂Fe₁₇Ns₃ was formed by the same method as an example 1. Subsequently, 10nm of Fe(s) was formed in this ambient atmosphere. A repeat Sm₂Fe₁₇N₃/Fe multilayer (ten laminatings) was produced for this process. Finally an ambient atmosphere was changed to Ar and 20nm of Ti was formed. This multilayer was heat-treated by 500 degree-Cx3h and 3x10⁻³Pa. Acquired magnetic properties were Br=1.6T, iHc=530 kA/m, and (BH) max=250.7 kJ/m³.

[0016] (Example 4) The Sm(Fe_{0.85}Co_{0.1}Mn_{0.05})₁₇N₃/Fe-Co multilayer was formed by the same method as an example 3. A protective coat of a multilayer was set to Cu₂₀nm. Acquired magnetic properties were Br=1.4T, iHc=620.5 kA/m, and (BH) max=230.6 kJ/m³.

[0017] (Example 5) A multilayer which has M layers and a hard magnetism layer which are shown in a table 1 by the same method as an example 1, and a soft magnetism layer was formed. Acquired magnetic properties are also shown in a table 1. Sample No.1, a thing for which 2 and 4 used a ThMn₁₂ mold intermetallic compound as a hard magnetism layer, and No.3 use Sm₂Co₇.

[0018]

[A table 1]

試料 No	積層膜				磁気特性		
	基板上	硬磁性層	軟磁性層	M層	Br (T)	iHc (kA/m)	(BH)max (kJ/m ³)
1	V	NdFe ₁₀ V ₂	Fe	V	1.2	475.3	210.3
2	W-V	NdFe ₁₁ Ti	Fe	W-V	1.25	350.6	223.8
3	Cu	Sm ₂ Co ₇	Fe-Co	Cu	1.0	506.5	170.4
4	Cr	NdFe ₁₀ VTi	Fe-Co	Cr	1.25	440.7	225.6

[0019] (Example 6) A multilayer which has M layers and a hard magnetism layer which are shown in a table 2 by the same method as an example 1, and a soft magnetism layer was formed. Acquired magnetic properties were also shown in a table 2.

[0020]

[A table 2]

試料 No	積層膜				磁気特性		
	基板上	硬磁性層	軟磁性層	M層	Br (T)	iHc (kA/m)	(BH)max (kJ/m ³)
5	Co-Pt	Nd _{0.7} Fe _{8.7} Co _{0.5} Al _{1.0} , sGa _{0.5} B	Fe-Co	Co-Pt	1.3	1070.8	207.5
6	Fe-Pt	Sm(Co _{0.73} Fe _{0.2} , sCu _{0.05} Zr _{0.015}) _{7.5}	Fe-Co	Fe-Pt	1.4	1175.8	240.3

[0021]

[Effect of the Invention] By this invention, magnetization is large and the outstanding hard magnetism thin film and outstanding exchange spring magnet which have a big maximum energy product are obtained.

[Translation done.]

(19) 日本国特許庁 (J P)

(12) 公開特許公報 (A)

(11) 特許出願公開番号

特開平9-266113

(43) 公開日 平成9年(1997)10月7日

(51) Int.Cl. ⁶	識別記号	庁内整理番号	F I	技術表示箇所
H 0 1 F 10/08			H 0 1 F 10/08	
C 2 2 C 38/00	3 0 3		C 2 2 C 38/00	3 0 3 D
H 0 1 F 1/147			H 0 1 F 41/22	
41/22			1/14	B

審査請求 未請求 請求項の数8 O L (全 5 頁)

(21) 出願番号	特願平8-75734	(71) 出願人	000005083 日立金属株式会社 東京都千代田区丸の内2丁目1番2号
(22) 出願日	平成8年(1996)3月29日	(72) 発明者	佐久間 昭正 埼玉県熊谷市三ヶ尻5200番地日立金属株式会社磁性材料研究所内
		(72) 発明者	新藤 幹夫 埼玉県熊谷市三ヶ尻5200番地日立金属株式会社磁性材料研究所内
		(72) 発明者	徳永 雅亮 埼玉県熊谷市三ヶ尻5200番地日立金属株式会社磁性材料研究所内
		(74) 代理人	弁理士 大場 充

(54) 【発明の名称】 硬磁性薄膜ならびに交換スプリング磁石およびその製造方法

(57) 【要約】

【課題】 大きな磁化を持つことで大きな最大エネルギー積を有する優れた硬磁性薄膜ならびに希土類系交換スプリング磁石およびその製造方法を提供するものである。

【解決手段】 硬磁性層と軟磁性層とが交換結合した複合構造からなり、厚さ1nm~700nmの硬磁性層と厚さ1nm~700nmの軟磁性層とが交互に積層された積層膜である硬磁性薄膜。

(2)

【特許請求の範囲】

【請求項1】 硬磁性層と軟磁性層とが交換結合した複合構造からなり、厚さ1nm～700nmの硬磁性層と厚さ1nm～700nmの軟磁性層とが交互に積層された積層膜であることを特徴とする硬磁性薄膜。

【請求項2】 硬磁性層が $RaTbNMcADdXe$ (R は Y を含む希土類元素のうち少なくとも一種、 TM は Fe 、 Co 、 Ni のうち少なくとも一種、 NM は Si 、 Ti 、 V 、 Cr 、 Mo 、 W のうち少なくとも一種、 AD は Al 、 Zn 、 Cu 、 Ga 、 Ge 、 Zr 、 Nb 、 Sn 、 Sb 、 Hf 、 Ta のうち少なくとも一種、 X は硼素、炭素または窒素のうち少なくとも一種で、 $5 \leq a \leq 18 \text{ at } \%$ 、 $65 \leq b \leq 85 \text{ at } \%$ 、 $0 \leq c \leq 20 \text{ at } \%$ 、 $0 \leq d \leq 8 \text{ at } \%$ 、 $0 \leq e \leq 15 \text{ at } \%$) なる組成を有する請求項1に記載の硬磁性薄膜。

【請求項3】 硬磁性層が $RaTbNMcADdXe$ の組成を有し、 $CaCu5$ 型、 $TbCu7$ 型、 $Gd2Co7$ 型あるいは $Ce2Ni7$ 型、 $ThMn12$ 型、 $Th2Zn17$ 型あるいは $Th2Ni17$ 型結晶構造の何れか一つあるいはこれらの複合体を主構造とする請求項1または2記載の硬磁性薄膜。

【請求項4】 軟磁性層の磁化の大きさが室温において1.3T以上である請求項1ないし3のいずれかに記載の硬磁性薄膜。

【請求項5】 積層膜の表面に、 M 層からなる保護膜を有する請求項1ないし4のいずれかに記載の硬磁性薄膜。

【請求項6】 厚さ1nm～700nmの硬磁性層と厚さ1nm～700nmの軟磁性層とが交互に積層された積層膜からなることを特徴とする交換スプリング磁石。

【請求項7】 積層膜の表面に、 M 層からなる保護膜を有する請求項6に記載の硬磁性薄膜。

【請求項8】 基板上に、773K(500℃)以下の基板温度で、軟磁性層と、硬磁性層を少なくとも1層以上成膜した後、773K(500℃)～1073K(800℃)の温度で熱処理することを特徴とする交換スプリング磁石の製造方法。

【発明の詳細な説明】

【0001】

【発明の属する技術分野】本発明は、小型モータ、磁気センサ、アクチュエータ等に応用される $R-TM-B$ 系硬磁性層と軟磁性層を積層させた多層構造の薄膜磁石ならびに $R-TM-B$ 系交換スプリング磁石およびその製造方法に関する。

【0002】

【従来の技術】エレクトロニクス機器の小型・軽量化に対応して、永久磁石材料の高性能化が進められている。現在、最高の磁石特性を有する $R-TM-B$ 系磁石の磁気特性を上回る可能性のある材料の一例として、交換スプリング磁石が挙げられる。交換スプリング磁石の保磁

2

力は、硬磁性相の磁化が軟磁性相の磁化を固定して、軟磁性相の磁化反転を妨げることによって発現する。十分な保磁力を得るためには、軟磁性相と硬磁性相が強く交換結合していることと、それぞれの相の大きさ(粒径)がナノレベルサイズであることが必要である。この交換スプリング磁石の製造方法は、超急冷法によってアモルファス薄帯を製造し、熱処理によって軟磁性相と硬磁性相が混合した多結晶を得る方法が主流である。

【0003】

【発明が解決しようとする課題】今後需要の増大が予想されるエレクトロニクス機器の磁石にはより小型、軽量化および高性能化が求められるため、現在の $Nd-Fe-B$ 系磁石より更に大きな磁化が要求されるようになり、その対策のための開発あるいは新しい磁石の探索が進められている。本発明は、大きな磁化を持つことで大きな最大エネルギー積を有する優れた硬磁性薄膜ならびに希土類系交換スプリング磁石およびその製造方法を提供するためである。

【0004】

【課題を解決するための手段】硬磁性相と軟磁性相の二相からなる超微細結晶組織で構成される永久磁石はCoe hoorn等(J.dePhys. vol. 49, p669(1988))やKneller等(IEEE Trans. Mag. vol. 27, p3588(1991))によって提案され、交換スプリング磁石と呼ばれている。これは、一般に磁化の大きい軟磁性相と保磁力の大きい硬磁性相とを組み合わせ、これらを交換相互作用により磁氣的に結合させることで高いエネルギー積を得ようというものである。一般に永久磁石材において、硬磁性相と交換結合する軟磁性相があると、逆磁界下で軟磁性相から先に磁化反転が始まり、保磁力低下の主要因となる。しかし、軟磁性相のサイズを磁壁幅以下に抑えると、逆磁界下における不均一磁化反転が抑制される。その結果、保磁力は主に硬磁性相の磁気異方性に支配され低下は抑えられる。一方、軟磁性相からより高い磁束密度 B を得るためには、軟磁性相の体積比を上げる必要があり、このためには一つの硬磁性相のサイズをできる限り小さくすればよい。硬磁性相のサイズはやはり磁壁幅以下であればよいが、あまり狭いと保磁力を維持するのが困難になるため磁壁幅程度に抑えるのが好ましい。磁壁幅は $\pi(A/K)^{1/2}$ (A :交換スティッフネス定数、 K :磁気異方性エネルギー)で見積もられるので、軟磁性相を Fe 、硬磁性相を $Nd2Fe14B$ とすると、それぞれ60nmおよび数nm程度となる。R.Skonski and J.M.D.Coey (Phys. Rev. B48(1993) p15812)によると交換スプリング磁石において、最大エネルギー積(BH) $_{max}$ が最も大きくなるときの硬磁性相の体積比 f_h は近似的に(1)式で与えられ、このとき最大エネルギー積は(2)式となる。

【0005】

【数式1】

50

(3)

$$f_h = \frac{\mu_0 M_s^2}{4 K_h} \quad (1)$$

(M_s: 軟磁性相の磁化、K_h: 硬磁性相の磁気異方性エネルギー)

$$(BH)_{max} = \frac{\mu_0 M_s^2}{4} \left(1 - \frac{\mu_0 (M_s - M_h) M_s}{2 K_h} \right) \quad (2)$$

(M_h: 硬磁性相の磁化)

【0006】一般に、Sm-CoやNd-Fe-B磁石の磁気異方性エネルギー-K_hは107J/m³程度であるのに対し、Fe等の軟磁性体のμ₀M_s²/4は106J/m³程度であるので、硬磁性相の体積比-f_hは10%程度あればよいことになる。従って、(BH)_{max}は主に軟磁性相の特性に支配され定量的にはμ₀M_s²/4に僅かな補正が加わる形となる。(2)式においてNd₂Fe₁₄Bを硬磁性相、Feを軟磁性相とした場合には、f_h=10%で、(BH)_{max}=0.8MJ/m³(100MG Oe)が期待される。以上のような特性を得るには、硬磁性相と軟磁性相が接触界面で充分な磁氣的結合を有し、それぞれの相厚が上述した磁壁幅程度に制御されている必要がある。本発明の対象となる積層膜はこのような制御が最も容易に実現され得る構造であると考えられる。

【0007】R-TM-NM-AD-Xからなる硬磁性層は耐食性が悪く、十分に酸化を抑制しないと希土類を含む金属間化合物が生成しにくくなったり、軟磁性相との交換結合が不十分となって保磁力が劣化する可能性が高い。本発明者等は、薄膜技術を応用することによって構造を制御しやすくし、保磁力を向上させ、薄膜化による酸化抑制のための保護膜を形成することによって保磁力の低下を防ぐことに想到した。したがって、本発明は、硬磁性層と軟磁性層とが交換結合した複合構造からなり、厚さ1nm~700nmの硬磁性層と厚さ1nm~700nmの軟磁性層とが交互に積層された積層膜である硬磁性薄膜である。本発明において、硬磁性層は、RaTbNbMcAdDdXe(RはYを含む希土類元素のうち少なくとも一種、TMはFe、Co、Niのうち少なくとも一種、NMはSi、Ti、V、Cr、Mo、W、のうち少なくとも一種、ADはAl、Zn、Cu、Ga、Ge、Zr、Nb、Sn、Sb、Hf、Taのうち少なくとも一種、Xは硼素、炭素または窒素のうち少なくとも一種で、5≤a≤18at%、65≤b≤85at%、0≤c≤20at%、0≤d≤8at%、0≤e≤15at%)なる組成を有する。硬磁性層は、CaCu₅型、TbCu₇型、Gd₂Co₇型あるいはCe₂Ni₇型、ThMn₁₂型、Th₂Zn₁₇型あるいはTh₂Ni₁₇型結晶構造の何れか一つあるいはこれらの複合体を主構造とすることができる。軟磁性層としては、磁化の大きさが室温において1.3T以上である軟磁性材料を

用いることが好ましい。また、本発明は、厚さ1nm~700nmの軟磁性層および厚さ1nm~700nmの硬磁性層を積層した希土類系交換スプリング磁石である。本発明において、軟磁性層と硬磁性層とを交換結合させるために、軟磁性層と硬磁性層を交互に積層して多層膜とすることが望ましい。また、軟磁性層および硬磁性層を積層した多層膜の表面にM層(Cr、Ti、W、Cu、V、Ta、FeMn、NiMn、NiO、FeO、CoO、Co-Pt、Fe-Ptのうち1種または2種以上からなる層)を形成し、軟磁性層と硬磁性層の酸化を抑制することが望ましい。

【0008】本発明において、硬磁性層は、RaTbNbMcAdDdXe(RはYを含む希土類元素のうち少なくとも一種、TMはFe、Co、Niのうち少なくとも一種、NMはSi、Ti、V、Cr、Mo、W、のうち少なくとも一種、ADはAl、Zn、Cu、Ga、Ge、Zr、Nb、Sn、Sb、Hf、Taのうち少なくとも一種、Xは、硼素、炭素または窒素のうち少なくとも一種で、5≤a≤18at%、65≤b≤85at%、0≤c≤20at%、0≤d≤8at%、0≤e≤15at%)なる組成を有する硬磁性薄膜であることが望ましい。Rとしては、特にNd、SmまたはPrの少なくとも1種を含むことが望ましく、Nd、SmまたはPrの一部をDyで置換してもよい。R-TM-NM-AD-Xからなる硬磁性層は、CaCu₅型、TbCu₇型、Gd₂Co₇型あるいはCe₂Ni₇型、ThMn₁₂型、Th₂Zn₁₇型あるいはTh₂Ni₁₇型結晶構造の何れか一つあるいはこれらの複合体を含み、膜厚は1~700nmとし、5~100nmがより望ましい。硬磁性層では、Rが5at%以下では十分な保磁力が発現せず、18at%以上ではTM成分が減少して(BH)_{max}とBrが減少する。NMの添加は希土類金属間化合物の結晶安定性に効果的であり、特にThMn₁₂型結晶の形成には不可欠となる。但し、20at%以上添加するとBrの著しい低下を招く。ADは形成された希土類金属間化合物の結晶粒の微細化、均一化に効果があり保持力の確保に効果的である。XはBrの増大に効果的であり、15at%以上では(BH)_{max}とBrが低下する。

【0009】R-TM-NM-AD-Xからなる硬磁性層の磁化は室温で通常1.3T以上であるため、交換スプリング磁石の優位性を得るためには、軟磁性層の磁化

(4)

5

の大きさは室温で1.3 T以上とし、更にバルクのR-Fe-B系磁石の特性を上回るには、1.5 T以上とするのが望ましい。室温における磁化の大きさが1.3 T以上の軟磁性材料としては、Fe: 2 T, Fe-Co: 2.3 T, Fe-N: 2.4 T等がある。軟磁性層は、その磁壁の幅から考えて、1~700 nmとし、5 nm~500 nmとすることが望ましい。硬磁性層と軟磁性層を交換結合させるために、軟磁性層と硬磁性層を交互に積層した多層膜を形成するが、積層順は軟磁性層、硬磁性層、軟磁性層、・・・軟磁性層と積層しても、硬磁性層、軟磁性層、硬磁性層、・・・硬磁性層と積層しても、軟磁性層、硬磁性層、軟磁性層、・・・硬磁性層と積層しても、硬磁性層、軟磁性層、硬磁性層、・・・軟磁性層と積層してもいづれでもよい。

【0010】軟磁性層と硬磁性層を交互に積層した多層膜の最外面にM層(Cr, Ti, W, Cu, V, Ta, FeMn, NiMn, NiO, FeO, CoO, Co-Pt, Fe-Ptのうち1種または2種以上からなる層)を形成し、軟磁性層と硬磁性層の酸化を抑制する。M層は、積層膜の表面全面に形成してもよいし、多層膜を挟むように、または片方に形成してもよい。M層は、基板と、多層膜との間、および軟磁性層と硬磁性層との積層膜上のいずれか一方に形成することによっても酸化抑制の効果は得られるが、表面全面あるいは多層膜を挟むように形成することにより軟磁性層と硬磁性層の酸化を十分抑制することができ、その結果、硬磁性層と軟磁性層の交換結合が強くなり、磁気特性の優れた多層膜を得ることができる。また、基板上にM層を成膜し、その上に軟磁性層と硬磁性層の多層膜を積層することによって、軟磁性層または硬磁性層の酸化抑制および基板との反応を防ぐという効果が得られる。M層の厚さは、これと隣接する硬磁性層あるいは軟磁性層との相互拡散により界面で合金あるいは化合物を形成しても十分にその機能を損なうことのないように5 nm~100 nm、望ましくは5~20 nmとする。

【0011】NiO, FeO, CoOは反強磁性絶縁体であるため、これをM層として用いれば、酸化抑制の効果に加え、磁化反転を抑えることで保磁力向上の効果を得ることができる。FeMn, NiMnも反強磁性体であるためこれをM層として用いれば、保磁力向上の効果を得ることができるが、他のM層構成物質に比し酸化防止効果が少ないので、基板と硬磁性層または軟磁性層との間に形成することが望ましい。また、Co-Pt, Fe-Ptは強い結晶磁気異方性を有する強磁性金属であるため、これをM層として用いれば酸化防止効果と保磁力増大の効果に加えて磁化の増大も期待できる。

【0012】硬磁性層の成膜時の酸化を抑制するため、硬磁性層は773 K (500℃)以下の基板温度で成膜することが好ましいが、その場合R-TM-NM-AD-Xからなる硬磁性層は結晶化せずにアモルファスとな

6

っており保磁力が発現しない。この場合、希土類金属間化合物の多結晶を得るために熱処理が必要である。熱処理温度は773 K (500℃)以下にすると化合物が結晶化しないので保磁力が発現せず、1073 K (800℃)以上にすると保磁力が急激に減少する。したがって、熱処理温度は773 K (500℃)から1073 K (800℃)が適当であるが、熱処理中の拡散による積層構造の乱れが少なく、かつが十分生成する、773 K (550℃)から923 K (650℃)が望ましい。

【0013】

【発明の実施の態様】

(実施例1)二極マグネトロンスパッタ装置の真空槽内を 8×10^{-4} Pa以下に排気し、Arガスを導入して 8×10^{-1} Paとし、まずTaをターゲットとして以下の成膜条件でM層としてTa膜を作製した。ガラス基板温度25℃、高周波投入電力200 Wとして成膜前に基板とターゲット間に取り付けられたシャッターを閉じて5分間予備スパッタによってターゲット上の酸化物を除去した。次にシャッターをあけて、成膜速度1.3 $\mu\text{m}/\text{h}$ でTaを10 nm成膜した。次に、SmCo5が硬磁性層となるよう成膜した。成膜条件は、高周波投入電力200 Wで、SmCo4.5ターゲットの表面酸化物除去のため20分間予備スパッタを行った。次に、SmCo5を成膜速度2.0 $\mu\text{m}/\text{h}$ で10 nm成膜した。引き続き真空を破らずに、Feターゲットに高周波電圧を印加してSmCo5と同条件でFe膜を10 nm成膜した。成膜速度は0.3 $\mu\text{m}/\text{h}$ である。これを交互に繰り返して、SmCo5とFeの多層膜(積層数10)を作製し、最後にV膜を20 nm作製した。得られたTa膜およびV膜で保護されたSmCo5/Fe多層膜を600℃×0.5 h、 3×10^{-3} Paで熱処理した。得られた磁気特性は $B_r = 0.95 \text{ T}$, $iH_c = 159 \text{ kA/m}$, $(BH)_{\text{max}} = 135 \text{ kJ/m}^3$ であった。また、得られた硬磁性薄膜に iH_c に相当する減磁界を印加してリコイル特性を調べたところ磁化の75%が復元するいわゆるスプリングバックが認められたことから、この磁性膜が交換スプリング磁石になっていることが確認された。

【0014】(実施例2)ガラス基板上にTiを20 nm成膜し、次に実施例1と同様の方法でSm-Co-Fe-Cu-Zr/Fe-Co多層膜(積層数10)を成膜した。最後に再度Tiを20 nm成膜した。硬磁性層はSm(Co bal. Fe 0.2 Cu 0.05 Zr 0.02)7、軟磁性層は70 wt% Fe-30 wt% Co組成である。得られた多層膜を600℃×0.5 h、 3×10^{-3} Paで熱処理した。得られた磁気特性は $B_r = 1.0 \text{ T}$, $iH_c = 120 \text{ kA/m}$, $(BH)_{\text{max}} = 155 \text{ kJ/m}^3$ であった。

【0015】(実施例3)ガラス基板上に実施例1と同様の方法でTiを20 nm成膜した。次に成膜雰囲気

50

(5)

7

窒素5%／Ar95%とに変更し実施例1と同様の方法で $\text{Sm}_2\text{Fe}_{17}\text{N}_3$ を10nm成膜した。次いで同雰囲気でFeを10nm成膜した。本プロセスを繰り返し $\text{Sm}_2\text{Fe}_{17}\text{N}_3/\text{Fe}$ 多層膜(積層数10)を作製した。最後に雰囲気をArに切り替えて、Tiを20nm成膜した。本多層膜を $500^\circ\text{C} \times 3\text{h}$ 、 $3 \times 10^{-3}\text{Pa}$ で熱処理した。得られた磁気特性は $B_r = 1.6\text{T}$ 、 $iH_c = 530\text{kA/m}$ 、 $(BH)_{\max} = 250.7\text{kJ/m}^3$ であった。

【0016】(実施例4)実施例3と同様の方法で $\text{Sm}_{10}(\text{Fe}_{0.85}\text{Co}_{0.1}\text{Mn}_{0.05})_{17}\text{N}_3/\text{Fe}-\text{Co}$ 多層膜を成膜した。多層膜の保護膜は Cu_{20} *

8

*nmとした。得られた磁気特性は $B_r = 1.4\text{T}$ 、 $iH_c = 620.5\text{kA/m}$ 、 $(BH)_{\max} = 230.6\text{kJ/m}^3$ であった。

【0017】(実施例5)実施例1と同様の方法で表1に示すM層、硬磁性層、軟磁性層を有する多層膜を成膜した。表1には得られた磁気特性も示す。試料No. 1, 2及び4は硬磁性層として ThMn_{12} 型金属間化合物を用いたもの、No. 3は Sm_2Co_7 を用いたものである。

【0018】

【表1】

試料 No	積層膜				磁気特性		
	蒸着順	硬磁性層	軟磁性層	M層	B_r (T)	iH_c (kA/m)	$(BH)_{\max}$ (kJ/m ³)
1	V	$\text{NdFe}_{10}\text{V}_2$	Fe	V	1.2	475.3	210.3
2	W-V	$\text{NdFe}_{11}\text{Ti}$	Fe	W-V	1.25	350.6	223.8
3	Cu	Sm_2Co_7	Fe-Co	Cu	1.0	506.5	170.4
4	Cr	$\text{NdFe}_{10}\text{VTi}$	Fe-Co	Cr	1.25	440.7	225.6

【0019】(実施例6)実施例1と同様の方法で表2 20※【0020】
に示すM層、硬磁性層、軟磁性層を有する多層膜を成膜
した。表2には得られた磁気特性も示した。 ※

【表2】

試料 No	積層膜				磁気特性		
	蒸着順	硬磁性層	軟磁性層	M層	B_r (T)	iH_c (kA/m)	$(BH)_{\max}$ (kJ/m ³)
5	Co-Pt	$\text{Nd}_0.7\text{Fe}_{0.7}\text{Co}_0.5\text{Al}_{1.0}\text{Ga}_{0.5}\text{B}$	Fe-Co	Co-Pt	1.3	1070.8	207.5
6	Fe-Pt	$\text{Sm}(\text{Co}_{0.73}\text{Fe}_{0.2}\text{Cu}_{0.05}\text{Zr}_{0.015})_{7.5}$	Fe-Co	Fe-Pt	1.4	1175.8	240.3

【0021】

【発明の効果】本発明により、磁化が大きく、大きな最 30

大エネルギー積を有する優れた硬磁性薄膜および交換スプリング磁石が得られる。